



DNR REMEDIATION & REDEVELOPMENT PROGRAM GUIDANCE FOR PUBLIC COMMENT



The Remediation and Redevelopment Program is seeking input on the publication below. Email the staff contact listed below to share feedback.

DOCUMENT TRACKING NUMBER

RR-0156

DOCUMENT TITLE

Guidance: Monitored Natural Attenuation (RR0156), Wis. Stat. § 292.12(5m)

BACKGROUND/SUMMARY

This publication provides guidance for persons who investigate, remediate and mitigate contaminated sites under Wisconsin Statute (Wis. Stat.) ch. 292 and Wisconsin Administrative (Wis. Admin.) Code chs. NR-700-799 and gives direction for characterization, assessment and monitoring of sites at sites where natural attenuation is under consideration as a possible remedial option for petroleum or chlorinated hydrocarbon contamination.

PUBLIC COMMENT PERIOD CLOSE DATE

Nov. 4, 2025

STAFF CONTACT & EMAIL ADDRESS (FOR PUBLIC COMMENTS)

DNRRRGuidance@wisconsin.gov

Please use subject line: "RR-0156 Comments"



Monitored Natural Attenuation Guidance

Wis. Stat. ch. 292, Wis. Admin. Code chs. NR 700-799

Purpose

This guidance is for persons who investigate, remediate and mitigate contaminated sites under Wisconsin Statute (Wis. Stat.) ch. 292 and Wisconsin Administrative (Wis. Admin.) Code chs. NR 700 - 799. It provides guidance for characterization, assessment and monitoring of sites where natural attenuation is being considered as a remedial option for petroleum or chlorinated hydrocarbon contamination. It focuses on the practical application and includes quick lookup tables to facilitate evaluation of site data, attenuation processes, geochemical indicators and contaminant trends. The information in this guidance may be used to support informed decisions using the regulatory framework, site investigation components, lines of evidence that support monitored natural attenuation as a remedy and monitoring recommendations to verify remedy effectiveness.

Contents

Definitions 2

Methods to Assess and Document the Effectiveness of Monitored Natural Attenuation 3

 Interpreting Geochemical Patterns 3

 Estimating Degradation Rates 4

 Using Multiple Lines of Evidence..... 4

 Characterizing the Contaminant Plume..... 4

 Determining Geochemical Conditions 4

 Conducting Microbiological and Isotopic Studies 4

 VOC Degradation..... 5

Monitored Natural Attenuation Reporting Requirements..... 5

Figures

Figure 1. Recommended Monitored Natural Attenuation Process

Tables

- Table 1. Recommended Monitoring for Chlorinated VOCs
- Table 2. Recommended Monitoring for Petroleum VOCs
- Table 3. Field and Laboratory Analytical Methods Summary Table – Monitored Natural Attenuation of Petroleum-Impacted Groundwater
- Table 4. Field and Laboratory Analytical Methods Summary Table – Monitored Natural Attenuation of Chlorinated-Impacted Groundwater
- Table 5. Recommended Monitoring for Chlorinated VOCs – Quick Reference
- Table 6. Recommended Monitoring for Petroleum VOCs – Quick Reference

Related Guidance

- *Guidance on Natural Attenuation for Petroleum Releases (RR-614)*
- *1-D Batch Flushing Model Spreadsheet for Use with Guidance on Natural Attenuation for Petroleum Releases (RR-614B)*
- *Regression Analysis – Concentration vs. Groundwater Elevation (RR-614C)*
- *Understanding Chlorinated Hydrocarbon Behavior in Groundwater (RR-699)*
- *Remediation Site Progress and Operation Maintenance Monitoring and Optimization Report (Form 4400-194)*

Wisconsin Department of Natural Resources (DNR) publications and forms referenced in this document include a number beginning with “RR-” or “4400-.” Locate these publications and forms by visiting dnr.wi.gov and searching for the number. Find additional DNR guidance on natural attenuation by visiting dnr.wi.gov and searching “natural attenuation.”

Natural attenuation generally refers to natural processes that reduce contamination in the environment without human intervention or enhancement. Natural attenuation processes may include dilution, dispersion, sorption, precipitation, volatilization, biotic and abiotic degradation and transformation.

When applied to contaminated sites, monitored natural attenuation is a complex remedy reliant on an understanding of the physical, geochemical, and biological processes that control the fate and transport of contaminants of concern. Monitored natural attenuation processes differ from site to site. Supporting data and documentation must be sufficient to justify its use as a remedy at sites in Wisconsin (Wis. Admin. Code § NR 722.13). Preparation of a conceptual site model (CSM) is recommended to provide a written and graphical representation of the natural processes, aquifer characteristics such as hydraulic conductivity, hydraulic gradient, and porosity to allow for the modeling of plume behavior over time. To obtain case closure for a site for which monitored natural attenuation is a selected remedy, a responsible party must demonstrate, among other things, that natural attenuation will bring the groundwater into compliance with Wis. Admin. Code ch. NR 140 groundwater quality standards within a reasonable period of time, and that the groundwater plume is stable or receding (Wis. Admin. Code § NR 726.05(6)(b)-(c)). When groundwater quality sampling is being conducted, results from a minimum of 8 successive quarterly rounds of sampling is required to demonstrate compliance with Wis. Admin. Code ch. NR 140 or the requirements of Wis. Admin. Code § NR 726.05(6), unless an alternative sampling schedule is approved by the DNR (Wis. Admin. Code § NR 726.09(2)(e)).

Definitions

Monitored natural attenuation means the reduction in the concentration and mass of a substance and its breakdown products in groundwater, due to naturally occurring physical, chemical, and biological processes without human intervention or enhancement. These processes include, but are not limited to, dispersion, diffusion, sorption and retardation, and degradation processes such as biodegradation, abiotic degradation and radioactive decay (Wis. Admin. Code § NR 700.03(38m)).

“Remedial action” or “remedy” means those response actions, other than immediate or interim actions, taken to control, minimize, restore, or eliminate the discharge of hazardous substances or environmental pollution so that the hazardous substances or environmental pollution do not present an actual or potential threat to public health, safety, or welfare or the environment. The term includes actions designed to prevent, minimize, stabilize, or eliminate the threat of discharged hazardous substances, and actions to restore the environment to the extent practicable and meet all applicable environmental standards. Examples include storage, disposal, containment, treatment, recycling, or reuse, and any monitoring required to assure that such actions protect public health, safety, and welfare and the environment (Wis. Admin. Code § NR 700.03(48)).

Methods to Assess and Document the Effectiveness of Monitored Natural Attenuation

Monitored natural attenuation is most often used to address petroleum and chlorinated volatile organic compounds (VOCs); however, under certain circumstances, site-specific conditions may support natural attenuation of some semi-volatile organic compounds (SVOCs) and inorganics. To determine the applicability of monitored natural attenuation, consider the target compounds, identified attenuation processes, site conditions, potential receptors, and restoration timeframe. Monitored natural attenuation can be incorporated into a site-specific CSM as it changes and expands with the site investigation.

Considerations for natural attenuation:

- Monitored natural attenuation is not appropriate as a sole remedy at a site with extensive groundwater contamination, an expanding or migrating plume, free product or potential threats to receptors.
- Comprehensive natural attenuation monitoring may not be necessary for sites with limited contamination and receptors.
- Additional data collection may not be necessary for sites where there is already a substantial data set that may be adequate to support a case-closure decision.
- While the focus of this document is monitored natural attenuation as a remedy, collecting data that evaluate natural attenuation may also be considered part of long-term monitoring for an active remedy (Wis. Admin. Code § NR 724.17).

Interpreting Geochemical Patterns

Patterns in the collected data within and between monitoring wells can help delineate the plume boundaries and support conclusions about the likely microbial processes occurring in a plume. The data may show patterns such as increased dissolved iron and methane and decreased nitrate and sulfate. Many of the recommendations for monitoring include assessment of the oxidation-reduction (redox) processes occurring in contaminated groundwater (see attached tables).

Collecting geochemical data during the initial site characterization and investigation phase can help determine which geochemical parameters are most relevant at a site. After the initial sampling event, the most relevant parameters may be selected for subsequent sampling.

Estimating Degradation Rates

An estimate of degradation rates is possible by using a semi-log plot of contaminant concentration versus time. The DNR's *Regression Analysis – Concentration vs. Groundwater Elevation* (RR-614C) tool may be used to estimate degradation rates. The tool estimates the degradation rates of dissolved phase petroleum hydrocarbons, and the calculations may also be applied to chlorinated hydrocarbons. Use of this tool is recommended when assessing the occurrence of natural attenuation.

Using Multiple Lines of Evidence

Demonstrating that monitored natural attenuation is a viable and appropriate remedy under Wis. Admin. Code ch. NR 722 relies on the collection and presentation of multiple types of data, including evaluation of contaminant plume characteristics, geochemical conditions and microbiological and isotopic studies. The collective data set is used to demonstrate the effectiveness of monitored natural attenuation to reduce contaminant concentrations.

Characterizing the Contaminant Plume

Stable or decreasing contaminant concentrations and groundwater plume margins over time are generally an indication that natural attenuation is occurring. When considering monitored natural attenuation as a remedial action option, the DNR recommends including evidence of a shrinking or stable plume in a remedial action options report to demonstrate it is a viable remedial alternative; having this information early on may facilitate efforts to demonstrate that monitored natural attenuation is an appropriate remedy that meets case closure requirements (Wis. Admin. Code § NR 726.05(6)(b)-(c)). Spatial or graphical analysis of the plume may be completed using a variety of visual aids. Typically, isoconcentration maps over time and graphs showing concentrations and trends from sampling data are used.

Determining Geochemical Conditions

The geochemical conditions present in the aquifer may indicate the degradation or attenuation of contaminants. Understanding the geochemical conditions of the aquifer is important to determine its capacity to degrade contaminants. Use the information in Tables 1 and 2 to determine if geochemical conditions are suitable for degradation and if degradation is occurring.

Conducting Microbiological and Isotopic Studies

Microbial studies can assess the ability for indigenous bacteria to degrade the contaminants. This type of testing can also document the isotopic fractionation that results from microbiologically mediated reductive dichlorination. Degradation products identified

during investigation may indicate the presence of suitable bacteria to promote further attenuation in a groundwater plume. Once degradation products are identified, collecting a baseline bacteria count may support monitored natural attenuation as a remedy or indicate the potential for aquifer augmentation (i.e., injections) to improve existing degradation processes.

VOC Degradation

Chlorinated VOCs tend to persist in the subsurface because the conditions needed for degradation of these chemicals are not always present. In addition, the degradation process produces other chlorinated VOCs as breakdown products. Even when natural attenuation and degradation occurs, it can be difficult to determine whether natural processes will be sufficient to remediate chlorinated VOCs to meet groundwater quality standards under Wis. Adm. Code ch. NR 140. Long-term monitoring must be performed as required under Wis. Admin. Code § NR 724.17. The general purpose for monitoring is to demonstrate and document that natural attenuation will bring groundwater into compliance with groundwater quality standards throughout the contaminant plume in a reasonable period of time, which is required to meet case closure criteria under Wis. Admin. Code § NR 726.05(6)(b).

Highly chlorinated VOCs (e.g., tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA)) are most readily degraded through reductive dechlorination. Reductive dechlorination may not be a complete process at some sites. Intermediate compounds, such as *cis*- and/or *trans*-1,2-dichloroethylene (cDCE or tDCE) or vinyl chloride (VC) may accumulate.

Less chlorinated compounds (e.g., dichloroethylene (DCE), dichloroethane (DCA), VC) may degrade through reductive dechlorination, but more readily degrade through oxidative processes. The less chlorinated compound serves as an electron donor with oxygen, nitrate, ferrous iron, or sulfate serving as the electron acceptor.

Monitored Natural Attenuation Reporting Requirements

Monitored natural attenuation is considered passive remediation. When monitored natural attenuation is being applied as a remedy before case closure, semi-annual operation and maintenance reporting to the DNR is required using the *Remediation Site Progress and Operation Maintenance Monitoring and Optimization Report* (Form 4400-194) (Wis. Admin. Code § NR 724.13(3)).

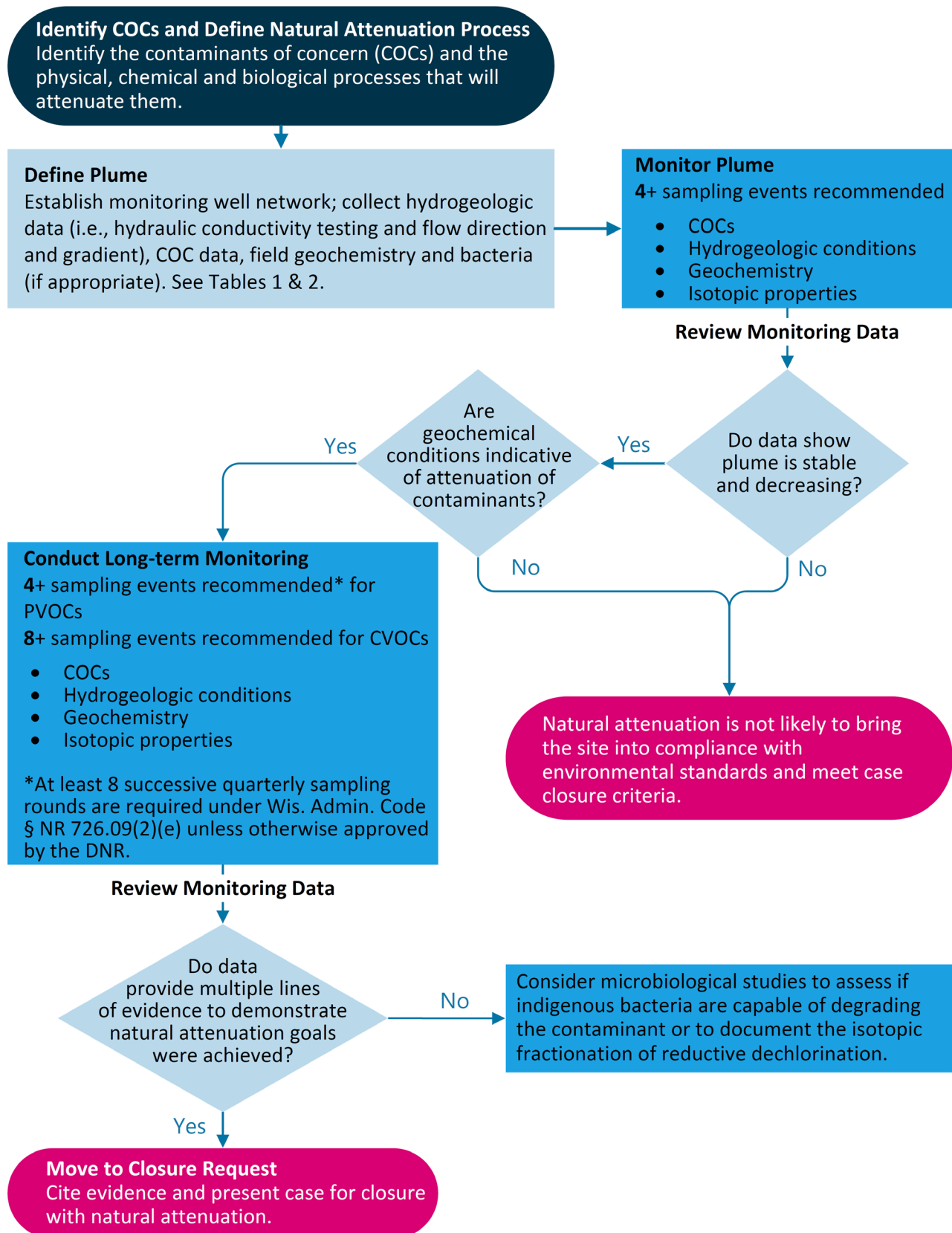
Figure 1. Recommended Monitored Natural Attenuation Process

Figure 2. Common Degradation Process

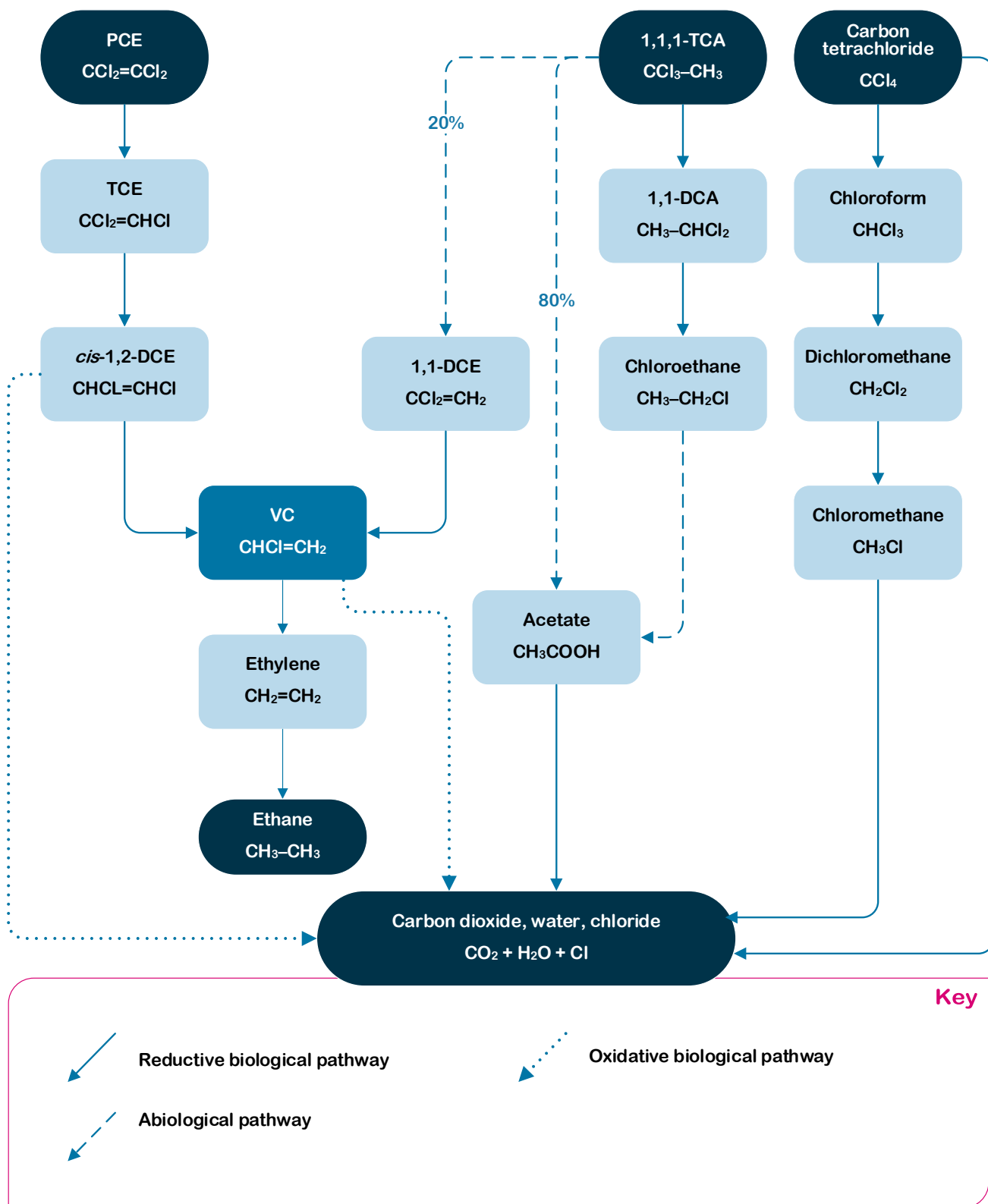


Table 1. Recommended Monitoring for Chlorinated VOCs

When chlorinated VOCs are the contaminants of concern, at a minimum, the DNR recommends monitoring for the following analytes and parameters:

COC Analysis

Full VOC list by EPA 8260

Identify all contaminants, including compounds originally discharged plus intermediate degradation products (see Figure 2). The full VOC list includes methyl-tert-butyl-ether (MTBE), tert-butyl formate (TBF) and tert-butyl alcohol (TBA).

Field Parameters

- **Specific conductance** - helps determine if the sample is collected from the same groundwater system. Look for an increased value over the background.
- **pH** - the optimal range for microbial activity is from 5 to 9 Standard Units.
- **Temperature** - at cooler temperatures, dechlorination can proceed at lower H_2 levels.
- **Oxidation reduction potential (ORP)** - reductive dechlorination typically requires an ORP of below -100 millivolts (mV), and optimal rates are often observed at ORP values between -200 millivolts (mV) and -300 mV.
- **Dissolved oxygen (DO)** - oxygen suppresses reductive dechlorination. *cis*-DCE, 1,1-DCE, 1,1-DCA, VC, methylene chloride, and chloromethane may degrade aerobically at DO concentrations greater than 1 milligram per liter (mg/L)

If data are indicative that monitored natural attenuation is viable, the DNR also recommends monitoring the following analytes and parameters:

Dissolved Gasses

- **Ethene (C_2H_4) by EPA 8015** - a daughter product of reductive dichlorination of VC.
- **Ethane (C_2H_6) by EPA 8015** - a daughter product of reductive dichlorination of 1,1,1-TCA. Also produced from ethene.
- **Methane (CH_4) by EPA 8015** - significant indicator of highly reduced groundwater conditions.

Anions/Inorganics

- **Nitrite (NO_2^-)/Nitrate (NO_3^-) by EPA 353.2 or 300** - Presence of NO_3^- suppresses reductive dechlorination under anaerobic conditions. The effect becomes stronger as nitrate concentrations increase.
- **Manganese (Mn^{2+}) by field colorimetric or EPA 6010B** - Reductive dechlorination may take place under iron reducing conditions. VC may be oxidized under these conditions.
- **Ferrous Iron (Fe^{2+}) dissolved & total (Fe^{3+}) by field colorimetric or EPA 6010B** -

Reductive dechlorination may take place under iron reducing conditions. VC may be oxidized under these conditions.

The following analytes and parameters may also be helpful to support monitored natural attenuation.

Bacteria

- **Dehalococcoides (DHC) bacterial count**
- **DHC Functional genes (bvcA, tceA, & vcrA)**

Quantify dehalococcoides and functional genes responsible for reductive dechlorination of PCE, TCE, DCE, vinyl chloride and other chlorinated compounds. Dehalococcoides concentration of $1.0\text{E}+04$ cells per milliliter (cells/mL) as a screening criterion to identify sites where biological reductive dechlorination will proceed at “generally useful” dechlorination rates. One sample at the start of groundwater monitoring is sufficient during site investigation activities.

Anions/Inorganics

- **Sulfate (SO_4^{-2}) by EPA 300** - Reductive dechlorination may occur under SO_4 reducing conditions. However, high levels of SO_4 can inhibit reductive dechlorination.
- **Sulfide (S^{2-}) by EPA 300** - Excess electron donor conditions can lead to high sulfide conditions that can inhibit the growth and metabolic activity of dechlorinating bacteria.
- **Chloride (Cl) by EPA 300** - From dechlorination. Environmental factors may interfere (e.g., road salt). Initial contaminant concentrations may be too low to detect a significant increase in Cl.
- **Total Organic Carbon (TOC) by SM 5310C** - Source of organic carbon necessary as driver for reductive dechlorination to proceed. Anthropogenic sources of carbon include BTEX.
- **Alkalinity by field colorimetric or lab titration** - A zone of increased alkalinity indicates biodegradation is either producing organic acids which lower the pH and solubilize carbonate from the soil or CO_2 is being produced.
- **Hydrogen by EPA 26a** -
 - Reductive dechlorination possible when hydrogen concentrations are greater than 1 nanomolar (nM).
 - Reductive dechlorination is typically not possible when the concentration of hydrogen is less than 1 nM.

Table 2. Recommended Monitoring for Petroleum VOCs

When petroleum VOCs are the contaminants of concern, at a minimum, the DNR recommends monitoring for the following analytes and parameters:

COC Analysis

Full VOC list by EPA 8260

Identify all contaminants, including compounds originally discharged plus intermediate degradation products (see Figure 2). The full VOC list includes methyl-tert-butyl-ether (MTBE), tert-butyl formate (TBF) and tert-butyl alcohol (TBA).

Field Parameters

- **Specific conductance** - helps determine if the sample is collected from the same groundwater system. Look for an increased value over the background.
- **pH** - the optimal range for microbial activity is from 5 to 9 Standard Units.
- **Temperature** - Oxygen solubility is dependent on groundwater temperature. Biodegradation rates may depend on temperature. An increase in temperature may be seen within the solute plume.
- **Oxidation reduction potential (ORP)** - Define regions of the plume under oxidizing and reducing conditions. Evaluate potential for biologically mediated redox reactions to occur. Helps validate DO measurements. Determine Eh values. ORP values typically range from +800 mV (strongly oxidizing) to -400 mV (strongly reducing). Lower ORP values are indicative of anaerobic conditions while higher ORP values indicate aerobic conditions.
- **Dissolved oxygen (DO)** - An inverse correlation of DO to BTEX concentrations indicates aerobic biodegradation is occurring. This relationship may also be expressed as depressed or non-detectable levels of DO throughout the plume. If levels of DO are depressed or non-detect while decreasing contaminant concentrations are being observed, it is strong evidence that microbial activity is occurring.

If data are indicative that monitored natural attenuation is viable, the DNR also recommends monitoring the following analytes and parameters:

Anions/Inorganics

- **Nitrate (NO_3^-) by EPA 353.2 or 300** - Decreased nitrate concentrations in anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons. If denitrification is occurring, nitrate concentrations will be lower within the petroleum plume and higher outside of the plume.
- **Manganese (Mn^{2+}) by field colorimetric or EPA 3010** - Decreased nitrate concentrations in anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons. If

denitrification is occurring, nitrate concentrations will be lower within the petroleum plume and higher outside of the plume.

- **Ferrous Iron (Fe^{2+}) dissolved & total (Fe^{3+}) by field colorimetric or EPA 3010** - Increased concentrations of Fe (II) may indicate Fe (III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons. If iron reduction is occurring, then concentrations of Iron III will be lower within the petroleum plume and higher outside of the plume.
- **Sulfate (SO_4^{-2}) by EPA 300-** Decreased sulfate concentrations in anaerobic portion of the plume may indicate use of sulfate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons. If sulfate reduction is occurring, then sulfate concentrations will be lower within the petroleum plume and higher outside of the plume.

The following analytes and parameters may also be helpful to support monitored natural attenuation:

Dissolved Gasses

- **Methane (CH_4) by field or lab GC** - Elevated concentrations may indicate anaerobic degradation using carbon dioxide as an electron acceptor. The presence of methane suggests BTEX degradation via methanogenesis.
- **Carbon Dioxide (CO_2) by field or lab GC** - Elevated carbon dioxide levels may indicate aerobic biodegradation, or depleted levels may indicate methanogenesis is occurring. Carbon dioxide data must be collected and reviewed carefully due to complex geochemical interactions.

Anions/Inorganics

- **Total Organic Carbon (TOC) by SM 5310C** - The fraction of organic carbon can influence the sorption of petroleum hydrocarbons and potentially reduce their bioavailability for microbial degradation.
- **Alkalinity by field colorimetric or lab titration** - A zone of increased alkalinity indicates biodegradation is either producing organic acids which lower the pH and solubilize carbonate from the soil or CO_2 is being produced.

Bacteria

- **Bacterial Count - Pseudomonas, Bacillus, Rhodococcus, and Acidovorax**
- **Functional Gene Detection - Oxygenases**

DNA sequencing or culture-based methods can be used to identify the type and abundance of petroleum-degrading bacteria present. Functional genes detected are an indication that the bacteria have the metabolic capability to break down petroleum hydrocarbons. The dominant bacteria can vary depending on environmental conditions.

Table 3. Field and Laboratory Analytical Methods Summary Table - Monitored Natural Attenuation of Petroleum-Impacted Groundwater

Parameter/Analyte	Method/Instrument	Purpose/Use
Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)	EPA Method 8260B (GC/MS)	Petroleum hydrocarbon quantification.
Naphthalene, 1- & 2-Methylnaphthalene	EPA Method 8260B/8270B	PAH quantification
Dissolved Oxygen (DO)	Field probe/meter	Indicator of aerobic biodegradation.
pH	Field meter	Geochemical indicator
Oxidation-Reduction Potential (ORP/Eh)	Field probe/meter	Redox condition indicator
Temperature	Field meter	Affects biodegradation rates
Conductivity	Field meter	General water quality
Nitrate/Nitrite	Field test kits/EPA Method 300	Electron acceptor for denitrification
Sulfate	Field test kits/EPA Method 300	Electron acceptor for sulfate reduction
Iron (Fe²⁺)	Field test kits (ferrozine method), EPA Method 200.7/200.8	Indicator of iron reduction
Methane, Ethene, Ethane	EPA Method 3810/8015	Byproducts of anaerobic biodegradation
Carbon Dioxide (CO₂), Alkalinity	Field titration (alkalinity), EPA Method 310.1 (alkalinity)	Byproduct of biodegradation
Chloride	Field test kits/EPA Method 300	Conservative tracer
Microbial Parameters	qPCR, PLFA, or other DNA/RNA methods	Optional; evidence of active biodegradation

Notes:

- Field measurements are critical for immediate assessment of site geochemistry and plume behavior.
- Laboratory analyses provide definitive quantification of contaminants and geochemical parameters to track attenuation processes and plume stability.

Table 4. Field and Laboratory Analytical Methods Summary Table - Monitored Natural Attenuation of Chlorinated-Impacted Groundwater

Parameter/Analyte	Method/Instrument	Purpose/Use
Chlorinated solvents (e.g., TCE, PCE, DCE, VC)	EPA SW-846 Method 8260B (GC/MS)	Quantify parent and daughter products
Major ions (Cl^-, SO_4^{2-}, NO_3^-, Fe^{2+}, Mn^{2+})	Ion chromatography, ICP, colorimetry	Evaluate geochemical conditions, redox status
Dissolved oxygen (DO)	DO meter (field probe)	Assess redox conditions for biodegradation
pH	pH meter (field probe)	Assess groundwater geochemistry
Oxidation-reduction potential (ORP)	ORP meter (field probe)	Assess redox environment
Temperature	Thermometer	Support geochemical data
Specific conductance	Conductivity meter	Assess ionic strength
Methane, ethene, ethane	EPA SW-846 Method 3810/8260B (GC/FID)	Evidence of reductive dechlorination
Hydrogen	Gas chromatography (field or lab)	Indicator of redox conditions
Microbial biomarkers (optional)	qPCR, DNA sequencing	Direct evidence of biodegrading organisms
Groundwater elevation	Water level meter	Define flow direction, gradient

Notes:

- VOCs (chlorinated solvents and breakdown products) are typically analyzed by EPA Method 8260B in a fixed laboratory.
- Geochemical indicators (DO, pH, ORP, major ions) are measured in the field and/or lab to assess conditions favorable for monitored natural attenuation.
- Methane and other gases are measured to provide evidence for reductive dechlorination.
- Microbial analyses are optional but provide direct evidence of biodegradation.
- Historical trend analysis and statistical evaluation of concentration data are essential for demonstrating attenuation.

The Wisconsin Department of Natural Resources (DNR) is committed to promoting diversity, fairness, equity and the principles of environmental justice. We ensure that we do not discriminate in employment, programs, decisions, actions or delivery of services. If you have questions or to request information in an alternative format (large print, Braille, audio tape, etc.), please contact us at 888-936-7463 or <https://dnr.wisconsin.gov/About/Nondiscrimination>

Table 5. Recommended Monitoring for Chlorinated VOCs - Quick Reference

Type	Analyte	Method*	Concentration in Source Zone or Change from Background	Explanation
Contaminants of Concern	Contaminant - full VOC scan	EPA 8260	See Common Degradation Pathways attachment for likely parent/daughter compounds.	Identify all contaminants, including compounds originally released plus intermediate degradation products. Full scan allows assessment of non-chlorinated compounds that may serve as electron donors.
Field Parameters	Specific Conductance	Field instrument (i.e. water quality meter)	Increase over background	General water quality parameter that helps determine if sample is collected from the same groundwater system.
	pH		5 < pH < 9	Optimal range for microbial activity
	Temperature			Affects microbial energetics. At cooler temps, dechlorination can proceed at lower H ² levels.
	Oxidation Reduction Potential (ORP)		<-100 mV	Reductive dechlorination likely.
	Turbidity		<50 mV	Reductive dechlorination possible.
	Dissolved Oxygen (DO)		< 0.5 mg/L	Oxygen suppresses reductive dechlorination. <i>cis</i> -DCE, 1,1-DCE, 1,1-DCA, VC, methylene chloride, and chloromethane may degrade aerobically.
Bacteria	Dehalococcoides (DHC) bacterial count	Lab specific	> 1.0E+04 cells/mL	Quantify Dehalococcoides and functional genes responsible for reductive dechlorination of PCE, TCE, DCE, vinyl chloride and other chlorinated compounds. Dehalococcoides concentration of 1.0E+04 cells/mL as a screening criterion to identify sites where biological reductive dechlorination will proceed at "generally useful" dechlorination rates. One sample at the start of groundwater monitoring is sufficient during site investigation activities.
	DHC Functional genes (BVC, TCE, & VCR)			
Dissolved Gasses	Ethene	EPA 8015	Present	Daughter product of reductive dichlorination of Vinyl Chloride.
	Ethane			Daughter product of reductive dichlorination of 1,1,1-TCA. Also produced from ethene.
	Methane		Increase over background	Indicates the most reduced groundwater conditions. VC accumulates at methane >0.5 mg/l.

Anions/ Inorganics (Select for appropriateness of MNA strategy)	Nitrite (NO ₂ ⁻)/Nitrate (NO ₃ ⁻)	353.2 or 300	< 1 mg/L	Presence of NO ₃ ⁻ suppresses reductive dechlorination. Anaerobic degradation of VC is typically observed under iron-reducing, sulfate-reducing, or methanogenic conditions.
	Manganese (Mn ²⁺)	Field colorimetric or EPA 6010B	Increase over groundwater along flow path	Reductive dechlorination may take place under iron reducing conditions. VC may be oxidized under these conditions.
	Ferrous Iron (Fe ²⁺) dissolved & total (Fe ³⁺)			
	Sulfate (SO ₄ ²⁻)	EPA 300	Decrease compared to background	Reductive dechlorination may occur under SO ₄ ²⁻ reducing conditions. However, high levels of SO ₄ ²⁻ can inhibit reductive dichlorination.
	Sulfide (S ²⁻)		Increase over background	Reductive dechlorination may occur. S ²⁻ may not be detected because of precipitation.
	Chloride (Cl ⁻)		> 2x background	From dechlorination. Environmental factors may interfere (e.g., road salt). Initial contaminant concentrations may be too low to detect a significant increase in Cl ⁻ .
	Total Organic Carbon (TOC)	SM 5310C	> 20 mg C/L	Source of organic carbon necessary as driver for reductive dechlorination to proceed. Anthropogenic sources of carbon include BTEX.
	Alkalinity	Field colorimetric or lab titration	> 2x background	Measures CO ₂ produced by microbial metabolism. Interference exists.
	Hydrogen	EPA 26a	> 1 NM	Reductive dechlorination possible. VC may accumulate.
< 1 NM			VC oxidized. Reductive dechlorination may not occur.	

*Other appropriate test methods may be available

Minimum data recommended to begin NA evaluation

Recommended minimum second tier if data is indicative of NA

Additional parameters as needed to fully define NA processes at a given site

Table 6. Recommended Monitoring for Petroleum VOCs - Quick Reference

Type	Analyte	Method*	Concentration in Source Zone or Change from Background	Explanation
Contaminants of Concern	Contaminant - full VOC scan	EPA 8260	See Common Degradation Pathways attachment for likely parent/daughter compounds.	Identify all contaminants, including compounds originally released plus intermediate degradation products. Full scan allows assessment of methyl-tert-butyl-ether (MTBE), tert-butyl format (TBF) and tert-butyl alcohol (TBA).
Field Parameters	Specific Conductance	Field Instrument (aka water quality meter)	Increase over background	General water quality parameter that helps determine if sample is collected from the same groundwater system.
	pH		5 < pH < 9	Aerobic and anaerobic biological processes are pH sensitive.
	Temperature			Oxygen solubility is dependent on groundwater temperature. Higher temperatures (near or above 7°C) enhance the microbial biodegradation by increasing metabolic and enzymatic activities.
	Oxidation Reduction Potential (ORP)		<-100 mV	Define regions of the plume under oxidizing and reducing conditions. Evaluate potential for biologically mediated redox reactions to occur. Helps validate DO measurements. Determine Eh values.
	Turbidity		<50 mV	In areas with high turbidity, the microbial degradation of petroleum is restricted due to the reduced oxygen concentrations.
	Dissolved Oxygen (D.O.)		< 0.5 mg/L	An inverse correlation of DO to BTEX concentrations indicates aerobic biodegradation is occurring. This relationship may also be expressed as depressed or non-detectable levels of DO throughout the plume.
Dissolved Gasses	Methane (CH ₄)	Field or lab GC	Increase over background	Elevated concentrations may indicate anaerobic degradation using carbon dioxide as an electron acceptor. The presence of methane suggests BTEX degradation via methanogenesis.
	Carbon Dioxide (CO ₂)			Elevated carbon dioxide levels may indicate aerobic biodegradation, or depleted levels may indicate methanogenesis is occurring. Carbon dioxide data must be collected and reviewed carefully due to complex geochemical interactions.
Anions/Inorganics	Nitrate (NO ₃ ⁻)	353.2 or 300	< 1 mg/L	Decreased nitrate concentrations in anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Manganese (Mn ²⁺)	Field colorimetric or EPA 6010B	Increase over groundwater along flow path	Mn ²⁺ ions and Mn ²⁺ oxidizing bacteria cooperate in degrading organic compounds by oxidizing Mn ²⁺ to higher oxidation states, which react to breakdown contaminants.
	Ferrous Iron (Fe ²⁺) dissolved & total (Fe ³⁺)			Increased concentrations of Fe (II) may indicate Fe (III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons
	Sulfate (SO ₄ ²⁻)	EPA 300	Decrease compared to background	Decreased sulfate concentrations in anaerobic portion of the plume may indicate use of sulfate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Total Organic Carbon (TOC)	SM 5310C	> 20 mg C/L	A higher content of organic carbon can enhance bacteria growth and stimulate the biodegradation process leading to the removal of petroleum hydrocarbons.
	Alkalinity	Field colorimetric or lab titration	> 2x background	A zone of increased alkalinity indicates biodegradation is either producing organic acids which lower the pH and solubilize carbonate from the soil or CO ₂ is being produced.

*Other appropriate test methods may be available

Minimum data recommended to begin NA evaluation
Recommended minimum second tier if data is indicative of NA

Additional parameters as needed to fully define NA processes at a given site